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(54) Title: NANOCOMPOSITES, PROCESS FOR MAKING THEM AND PRODUCTS MADE FROM THEM

(57) Abstract: Nanocomposite material which comprises a plastic matrix consisting of polyolefin and a mineral component in nanoparticles. The mineral component is Montmorillonite, in particles the major part of which have the shape of platelets of a thickness of the order of magnitude of nanometers. The length and breadth of the Montmorillonite platelets may vary from 1.5 m down to a few tenths of 1 m. The Nanocomposite material may be formed into a product having at least one direction of orientation, wherein the Montmorillonite platelets are mainly parallel or sub-parallel to the direction of orientation.

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## NANOCOMPOSITES, PROCESS FOR MAKING THEM AND PRODUCTS MADE FROM THEM

### Field of the Invention

This invention relates to nanocomposites constituted by a matrix predominantly of a polyolefin polymer having mineral platelets distributed therein and having improved physical properties, and to a process for making them. It further relates to plastic products made of such composites. In particular, the products may have an oriented structure, such as in containers or sheets, and the mineral platelets may be prevalently oriented parallel to the orientation of the products, e. g. parallel to a container axis or a sheet surface, rendering the product substantially liquid and/or gas proof.

### Background of the Invention

The art is constantly concerned with improving the physical properties of plastic products. In recent years plastic materials of a new type, called "nanocomposites", has been proposed, which consists of mixtures of thermoplastic polymers and mineral components and are intended to obtain improved mechanical and thermal properties. The term "nanocomposites" derives from the fact that the mineral components are in small particles, the dimensions of which can be measured in nanometers. This term, however, is often improperly applied when the mineral components, while very small, considerably exceed the nanometer dimension range. Various nanocomposite materials have been proposed, in which the polymers are nylon, particularly nylon 6, polyethylene, polypropylene, polycarbonates, polybutylene or methyl methacrylate. However fully satisfactory nanocomposites having a polyolefin matrix for molded containers have not been developed so far.

A type of products to which this invention is particularly, but not exclusively, directed, is constituted by containers, especially for aggressive liquids. All such containers proposed so far do not have the physical properties desired or/and require an excessive amount of mineral components, which is negative both from the viewpoints of the workability and physical properties of the material and from that of its cost. In particular, the art has not provided containers or differently shaped barriers made of nanocomposites, that are entirely liquid-proof, especially to aggressive organic liquids, and are gas-proof to their vapors, and can be made by standard shaping processes.

Certain processing methods, widely used in the plastic art, impart to products an oriented structure. Such methods are, for instance, extrusion or calendering. Processing methods by which thermoplastic polymers may be formed into hollow products, such as containers, include extruding the polymer and expanding the extruded tubular structure to conform to the inner surface of a mold by applying internal gas pressure. This process will be briefly referred to herein as "extrusion blow-molding". In a similar process, the thermoplastic polymer is injected into a mold and the injected polymer is conformed to the inner surface of the mold by the application of internal gas pressure. This process will be briefly referred to herein as "injection blow-molding". Containers are often made by extrusion blow-molding or injection blow-molding.

Thermoplastic polymers that are particularly important, because of their workability, low cost and high qualities of the products made from them, are the polyolefins, particularly high density polyethylene (hereinafter, HDPE) and polypropylene (hereinafter, PP). The art, however, has not succeeded so far in producing fully satisfactory nanocomposites having a polyolefin matrix. For example, it has not succeeded in producing polyolefin nanocomposite containers that are completely non-permeable, at

least at room temperature, to the aggressive liquids that are often stored in polyolefin containers and to their vapors.

It is therefore a purpose of this invention to provide nanocomposites that have a polyolefin matrix.

It is another purpose to provide products made of such nanocomposites.

It is a further purpose to provide oriented products made of such nanocomposites, wherein the mineral nanoparticles have an orientation corresponding to that of the products that contain them.

It is a still further purpose to provide such oriented products that are containers.

It is a still further purpose to provide such containers that are completely liquid-proof at or about room temperature, against the seepage of liquids, particularly aggressive and/or organic liquids.

It is a still further purpose to provide products made of such nanocomposites, which have improved mechanical and/or thermal properties, in particular such properties as impact resistance, ductility, dimensional stability in the manufacturing process, and thermal stability.

It is a still further purpose of the invention to provide products, particularly oriented products, made of nanocomposite materials with a polyolefin matrix, in which the percentage of mineral component is low, e.g., 1-5 wt%.

It is a still further purpose to provide products made of such nanocomposites that are chosen from among parts and/or accessories for

the automobile industry, plastic molded fuel tanks, parts of electronic devices, transparent products for the optical industry, and sheet and multisheet products.

It is a still further purpose to provide such nanocomposites that can be molded by standard processes and equipment to products having high mechanical and thermal properties.

It is a still further purpose to provide a process for the manufacture of oriented products, such as containers.

It is a still further purpose to provide a process in which the oriented product is shaped by blow-extrusion or blow-molding.

It is a still further purpose of the invention to achieve all the aforesaid purposes by the use of raw materials that are readily available.

Other purposes and advantages of the invention will appear as the description proceeds.

### Summary of the Invention

According to the invention, a composite material is provided which comprises a plastic matrix consisting of polyolefin, although minor amounts of modified polyolefins and/or different plastics may be, and preferably are, included, as will be hereinafter explained. The composite material comprises a mineral component in nanoparticles. Said component is preferably Montmorillonite, mostly in particles having the shape of platelets, one dimension of which – the thickness – is of the order of magnitude of one nanometer ( $10^{-9}$  meter), although particles of Montmorillonite having a greater thickness may be present. The length and breadth of the particles ranges generally from 1.5  $\mu\text{m}$  down to a few

tenths of 1  $\mu\text{m}$ . In finished, oriented products, the Montmorillonite platelets are mainly, though in general not completely, parallel or sub-parallel to the direction of orientation of the product. If the product is a container, they are parallel or sub-parallel to the lateral surfaces of the container, viz. to the surfaces of greater area, which are the most likely to cause significant leakage. Since containers typically have an axis of symmetry or quasi-symmetry, it may be said that, typically, in containers the platelets are mainly parallel to said axis. If the product is a sheet or a multisheet structure, the Montmorillonite platelets are mainly, though in general not completely, parallel or sub-parallel to the sheet surfaces. The amount of the Montmorillonite platelets is preferably from 1-5 wt% total weight of the composite, it being obvious that the finished product may comprise parts that are not made of the plastic composite. In molded parts that are solid and have no axis of symmetry the platelets may have a partial or a random orientation.

Containers will be described herein as examples of products obtained from embodiments of the invention, but no limitation is meant thereby as to the scope of the invention. More particularly, containers having a circular cross-section will be described for purposes of exemplification, but although this is a common shape of containers, the invention is not limited to them and comprises any shape of container. The containers may be cylindrical and have a circular cross-section, or a different cross-section that is symmetrical with respect to an axis, or a non-symmetrical cross-section. Also, preferred processes of making containers, viz. extrusion blow-molding or injection blow-molding, will be referred to hereinafter for purposes of description and not of limitation.

Since a polyolefin will be the main component of the plastic composites of the invention, it is called herein "the matrix". Besides the mineral component, additional materials may be compounded with the matrix.

They may be modified polyolefinic materials or different polymers, as will be hereinafter explained. The matrix is typically made of polypropylene (PP) or polyethylene (PE). The polyethylene used for difficult application, such as containers for aggressive chemicals, is preferably high-density polyethylene (HDPE), but medium- or low density polyethylenes are also comprised as matrix in the invention. Additional polymeric materials, that may be mixed in the composite with the matrix, include, for example but not exclusively, functionalized polyolefins, particularly polyolefins grafted with maleic anhydride, and/or polyamides, in particular nylon 6 and nylon 12. Other components may be compounded with the matrix as long as they are suitable for the purposes that will be explained hereinafter in describing the process of the invention. The composite materials, comprising polyamides as additional polymeric materials, are a particular aspect of this invention. Preferably, the polyamides are present in an amount of from 5 to 10 wt% of the whole polymeric material.

Montmorillonite is available on the market in untreated form, viz. as virgin powder. In this form, the Montmorillonite exists in particles, each of which is a stack of platelets held together by strong attractive bonds, particularly by electrostatic forces. Such structures are known as "galleries", and will be so called hereinafter. The formation of the galleries into platelets, for the purposes of this invention, must satisfy two requirements. The first requirement is that it should reduce the attraction between platelets, resulting in an expansion of the distance between adjacent platelets from, for instance, about 3.5 nanometers to, for instance, about 20 nanometers. This first requirement is achieved by a process known as intercalation. The intercalation, however, is not successful for the purposes of this invention unless it produces in the platelets a condition that will permit the polymer of the matrix to satisfy the second requirement that is known as exfoliation or delamination, and consists in the separation of the platelets from one another, so that they

may assume positions and orientations different from one another. It is however not essential that all the Montmorillonite be affected by the intercalation and the exfoliation. Part of it – as much as 50 wt% in some cases – may remain in the form of virgin galleries or of galleries that have been intercalated and exfoliated only in part.

Montmorillonite is also available in the market as powder that has undergone an intercalation treatment. However, the Montmorillonite so treated, that is present in the market or has been described in the art, is not suitable for use in this invention, because it is not such the polyolefins of the matrix may exfoliate it in the process of this invention. The Montmorillonite intercalated according to the invention is a new product and is, as such, an aspect of this invention. It has better intercalation capabilities in terms of inter-layer D-spacing distance, measured by SAXS (X-ray method) and better compatibility with various polymers.

The invention also provides a process for making nanocomposite plastic material, which comprises the following steps:

- a) providing a polyolefin material;
- b) providing virgin Montmorillonite;
- c) subjecting the Montmorillonite to intercalation;
- d) preferably, mixing the intercalated Montmorillonite with a compatibilizer as hereinafter defined, to form a concentrate; and
- e) compounding the resulting mixture with the said polyolefin material, resulting in the separation of the Montmorillonite platelets from one another, viz. in their exfoliation.

The aforesaid concentrate is also an aspect of this invention.



Additional, the invention provides a process for making products from the aforesaid components, which comprises the addition, to said steps a) to e), of a further step f): forming the resulting compound into a product.

The intercalation of the Montmorillonite to bring it to such a condition that it may later be exfoliated and compounded with the matrix polyolefin, or, preferably, with a compatibilizer, is preferably carried out with an epoxy resin, such as bisphenol A, though other intercalators, such as silanes, may be used. The compound used to produce intercalation - the "intercalator" - must be capable of insinuating itself between the platelets of the Montmorillonite galleries and to interact with the attractive forces that exist in the galleries to distance the platelets from one another, but must also be capable of the interconnecting with the compatibilizer, hereinafter to be described. In order to become insinuated between platelets, the intercalator must be brought to a condition of low viscosity. This is achieved preferably by applying it in solution, more preferably in an organic solvent, e.g. acetic acid or chloroform, this latter being preferred if the intercalator is an epoxy resin. A typical intercalation treatment consists therefore in mixing the virgin Montmorillonite (after an initial drying, if required) with chloroform for, e.g., 24 hours, drying it at least partially, and immersing it in a chloroform solution which contains 5 wt% of epoxy resin. In general, however, intercalation can be carried out with compounds other than epoxy resin, as long as they have low viscosity and are capable of loosening the attractive bonds between platelets. But these properties are not sufficient to produce intercalation that is adequate as a step of the process of this invention. Not all compounds having the said properties can be used in the intercalation stage of the invention, unless they are effective in promoting efficient exfoliation at a later stage of the process. The intercalation process increases the distance between platelets from a value that is typically 3.5 nm and anyway less than 10 nm to a value of about 20 nm.

The next preferred step of the process of the invention is the creation of a concentrate, which could not be properly called a master batch, because it comprises not the same polyolefin that constitutes the matrix of the final composite, but is mixture of intercalated Montmorillonite with a compatibilizer, which is preferably a polyolefin grafted with a functional compound that will permit it to penetrate between the platelets that have undergone the intercalation. The preferred compatibilizer is a polyolefin grafted with maleic anhydride. The amount of compatibilizer used is 5 to 10 wt% of the amount of the polymer matrix of the final composite.

The concentrate is to be mixed with the polymer of the matrix. As will be explained hereinafter, in some cases this is done by a separate compounding, while in other cases such compounding may be omitted and it is possible and preferred to mix the concentrate directly with the matrix polymer and subject the mixture to the operation by which the final product is formed. Additionally, in an embodiment of the invention, another polar compound compatibilizer, preferably based on a nylon, intercalated with Montmorillonite, can be added to the mixture of matrix polymer and intermediate stabilizer, also in a quantity, e.g., from 5 to 10 wt% of the amount of the matrix polymer.

The final operation – the formation of the product – can be carried out in many ways, depending particularly on the desired product, e.g. by extruding, molding by any of the known molding processes, by extrusion blow-molding or injection blow-molding in the case of a hollow product, etc. Though the compounding, resulting in exfoliation, and the formation of the product are indicated hereinbefore as separate and consecutive stages of the process, they may constitute a single stage if the compounding occurs concurrently with the formation of the product, e.g. when this latter is effected by extrusion or extrusion blow-molding. In other cases, e.g. if the

product is formed by conventional injection molding, its formation may have to be preceded by a separate compounding step.

### **Brief Description of the Drawings**

In the drawings:

- Fig. 1 schematically illustrates the chemical structure of Montmorillonite clay;
- Fig. 2 schematically illustrates the physical structure of Montmorillonite galleries;
- Fig. 3 schematically illustrates the intercalation stage;
- Fig. 4 schematically illustrates an exfoliation process;
- Fig. 5 schematically illustrates how the presence of oriented platelets opposes the seepage of liquids through a film; and
- Figs. 6 to 11 illustrate the reduced seepage of liquids from a container according to the invention.

### **Detailed Description of Preferred Embodiments**

In preferred embodiments of the invention, the nanocomposites can be used to produce a variety of final products. The following final products may be particularly mentioned:

containers for organic liquids, and/or aggressive liquids;

various parts and accessories for the automotive industry, including, e.g., parts of the motor, accessories for the seats of the driver and of the passengers and molded fuel tanks;

thin sheets useful as barriers against gases and vapors for use, e.g., for packaging and storing various products;

articles that are exposed to heat and need to be heat-stable;

coatings for various structures;

transparent products for the optical industry that have a high ratio of strength to weight;

parts of motors and electric devices that require high heat stability;

sheet materials having high anti-static properties;  
flame-retarded products;  
electrical parts that must be stable under exposure to ultraviolet radiation.

The structure of natural Montmorillonite is characterized by agglomerates of thin flat platelets. The shape and surface area of the platelets varies but their thickness is essentially uniform and is in the order of one nanometer. The ratio of thickness to length varies between 300 to 1500 and one gram of the platelets has a surface area of approximately 750 square meters. The molecular structure of a platelet of Montmorillonite is composed of an octahedral shaped alumina plate that is located between two parallel tetrahedral plates of silica.

Fig. 1 schematically shows the chemical structure of the agglomerate of platelets in Montmorillonite. In natural Montmorillonite there occurs an exchange of cations on the surface of the platelets. Generally cations of aluminum ( $\text{Al}^{+3}$ ) are replaced with cations of magnesium ( $\text{Mg}^{+2}$ ). This results in a net negative charge in the platelets which is neutralized by cations such as sodium, lithium, magnesium, calcium, or potassium which undergo dehydration and enter the space between the platelets.

Fig. 2 schematically shows the agglomerate structure with the cations between the layers of the stack. The agglomerate is very densely spaced with the space between layers dependent on the size of the cations and on the order of tenths of a nanometer in virgin Montmorillonite. The agglomerate is held together by the strong attractive forces between the negative charge on adjacent platelets and the cations in the gallery.

In order to accomplish the purposes of this invention, it is necessary to separate at least part of the layers of the agglomerate and obtain single

platelets of the Montmorillonite. This is accomplished in a two stage process. In the first stage, the intercalation, the height of the gallery is increased by chemical processes, thus reducing the attractive forces between the plates. In the second stage, the exfoliation, the attractive forces are overcome allowing the plates to separate. Exfoliation can be accomplished either a chemical or mechanical process or by a combination of the two.

Intercalation is carried out by replacing the cations in the gallery with other ions or molecules. One consideration is the size of the replacement molecule which determines the height of the gallery and also influences the strength of the force holding the plates together. It has been found that this height must be at least 1.7 nanometers in order for exfoliation to take place. Another factor that must be taken into consideration is that the final stability of the polymer matrix containing the Montmorillonite platelets will only be established if the platelets are strongly attached to the polymer.

A characteristic of the virgin Montmorillonite is that the platelets are hydrophilic, making them incompatible with most of the known polymers. To overcome this difficulty, organic molecules with suitable hydrophobic functional groups are used as intermediaries. They are introduced into the galleries, replace the cations that are present, and are attached to the platelets by ionic bonds. This modification of the surface allows the platelets of Montmorillonite to interact with the polymer in the process of producing the nanocomposite. In making this modification, there is the utmost importance to the strength of the connection of the intermediary to the surface of the platelet.

A second method of modifying the surface of the platelets is to leave the sodium ions in place in the galleries and to make use of the dipole induced

on the back side of the sodium that is trying to balance the negative charge on the alumina plate. The partially induced dipole on the sodium can interact with a partial negative dipole to anchor the intercalator to the platelet surface. Functional groups that possess a negative dipole include alcohols, carbohydrates, esters, amines, and ethers. Depending on the organic molecule chosen as an intercalator, a distinct complex will be formed with the platelets. The type of intercalator and the quantity introduced into the gallery will determine the distance between layers of the Montmorillonite. As the distance grows, the force holding the structure together diminishes until the point at which placing the nano-clay into the matrix of a polymer and applying mechanical shearing forces will cause the plates of the nano-clay to undergo exfoliation.

Fig. 3 illustrates the principles of the chemical processes involved in intercalation. Many different molecules can be used as intercalates to prepare the Montmorillonite for interaction with the polymer.

In a preferred embodiment of this invention, an epoxy resin such as bisphenol A is used as an intercalator. In order to introduce the epoxy resin into the galleries of the agglomerate, it is necessary to reduce the viscosity of the resin. This can be accomplished by applying it as a solution of concentration 5 to 10 wt% in chloroform.

There are two ways to perform the exfoliation step. In the first method, an appropriate intercalator is introduced into the galleries of the Montmorillonite. This intercalator must be capable of expanding the galleries enough to allow polymer macromolecules to enter the gallery. During the polymerization reaction, the space between the layers of the Montmorillonite is further increased until the force holding the structure together is so weakened that exfoliation takes place. The intercalator also

must have a functional group that can interact with the polymer during the reaction and effectively link the platelets to the polymer.

Fig. 4 schematically illustrates the chemical process that causes the exfoliation to take place and results in the creation of the nanocomposite. Nanocomposites produced in this way have improved mechanical properties when compared to their polymer matrix, which render them superior to said matrix, but their resistance to seepage of liquids and gases is not optimal, due to the random orientation of the clay platelets in the polymer matrix. However, when said resistance is an essentially desired property, the final product is made by extrusion or injection processes and the shearing forces that are present in such processes cause delamination of the layers in the Montmorillonite and assist in the exfoliation process. As a consequence, the platelets are distributed in parallel layers throughout the polymer matrix, so that they become oriented with their surface areas in planes parallel to the surfaces through which seepage is most likely to occur, such as e.g. the sides of a container. Fig. 5, which schematically shows the tortuous path that a liquid or gas molecule would have to take to pass through a film in which the platelets are oriented, e.g. the wall of a container, shows why the permeability of the nanocomposite is less than that of the matrix polymer alone.

The following examples are illustrative and not limitative. The process of the examples is divided into four steps, which will be successively described. In the first step virgin Montmorillonite powder is subjected to intercalation. In the second step the powder obtained from step 1 is mixed with compatibilizer polymers and compounding is carried out to produce a concentrate. In this step intercalation is completed and partial exfoliation is effected. The third stage is a melt blending stage in which the concentrate or concentrates of the second step is/are compounded with the polyolefinic matrix and a complete exfoliation takes place. In the fourth

and final step, a melt of the mixture obtained from the third step is subjected to a combined process of elongation and shear which produces the orientation of the mineral particles. Said four steps will now be described in detail.

#### Step 1

Fresh Montmorillonite powder, type "Cloisite Na" (Ex. Southern Clay products Inc.) is dried at 120-140°C, without vacuum, for 5-6 hours. The dried powder is then immersed in a polar solvent at a ratio of 500 gr solvent for 100 gr of powder. The solvent is either chloroform and/or methanol depending on the active agent later detailed. The solution is stirred until a suspension ("solution A") is obtained. This suspension is kept at room temperature for at least 12 hours.

In parallel, a surface-active agent ("solution B") is produced from the following components:

One. Epoxidized Bis-phenol A resin (Epon 1001, or Epon 1009, Ex. Shell Chem.), 5-10 % Wt in chloroform.

Two. Epoxy Silan (Silan GLYMO, Ex. HULS Co.), 5-10 % Wt in methanol.

The dissolving of both agents was carried out by mixing at room temperature or up to 50°C.

Solution B is then added into solution A, in such a way that 5-10 gr. of active agent are added for each 100gr of "Cloisite Na". The solution is mixed in a stirring vessel at room temperature for 5 hours. Then the vessel including the solution is transferred into ultrasonic bath, for 1-hour high frequency vibration treatment.



A first drying begins by evaporating the solvent at 50-60°C while stirring, until a solid powder pile is formed. The drying is completed by laying the above pile on a flat tray, at room temperature for 12 hours and then at 80-100°C for 3-4 hours. At this stage, mineral or ceramic powder particles in an intercalated state have been created.

### Step 2

The powder from step 1 is subsequently introduced into carrier polymers to form a concentrate, later to be compounded in the polyolefin (PE or PP) matrix, of various compositions of the following types:

- a. HDPE-g-MAH containing 1% maleic anhydride graft (Polybond 3009, Ex. Uniroyal, Fussabond MB100D, Ex. DuPont)
- b. PP-g-MAH containing 0.5% maleic anhydride graft ( Polybond 3035, Ex. Uniroyal, Fussabond MD-511, Ex. DuPont).
- c. LLDPE-g-MAH containing 1% maleic anhydride (Fussabond MB 226, Ex. DuPont).
- d. PA6 (Polyamide 6), high molecular weight, (Ultramid B5, Ex. BASF, Grilon F50, Ex. EMS).

With the first three polymers the intercalated powder is mixed to a concentration of 20-25 wt%, and with the last polymer to a concentration of 5-10 wt%.

The compounding process is performed in melt phase, by extrusion in either bi-screw compounder or one-screw Boss compounder. The powder is introduced only after the polymer is melted (in the last third of the process). In each of the said compounding steps, are added 1500 ppm of a thermal stabilizer(anti-oxidant), for the first three polymers (polyolefins) Irganox 1010, Ex. Ciba-Geigy, and for the last one (polyamide) Irganox B225, ex. Ciba-Geigy. The compounded particles thus obtained are then dried by dry hot air (80-90°C) for about 5 hours.

### Step 3

This step can be performed by two different approaches, depending on the polymer matrix and the processing mode for the final product.

One) In the case of processing to form containers by extrusion/blowing based on HDPE, the compositions, containing the compounded powder and the HDPE matrix are as follows:

HDPE-high molecular weight grade (Marlex TR571 or Marlex TR512, Ex. Philips 66) 85%.

HDPE-g-MAH (containing 20-25% of nano powder) - 10 %.

PA6 (containing 5-10% of the nano powder) - 5%.

Two) In the same case as a), about the same compositions are used, but with the following variations:

HDPE- 85%

HDPE-g-MAH (nano)- 5%

PA6 (nano) – 10%

Three) In the case of processing to form containers by extrusion/blowing based on PP, there are introduced into the inlet of the extruder controlled amounts of concentrates/compounds that contain the nano powder particles, together with the matrix (PP), in the following amounts:

PP random copolymer (Capilen QE73B, Ex. Carmel, or R520Y, Ex. SK Corp) – 85%

LLDPE-g-MAH (containing 20-25% nano powder) – 10%

PA6 (containing 5-10% of nano powder) – 5%

Four) In the same case as c), about the same composition is used, but with the following modifications:

PP random copolymer - 85%

LLDPE-g-MAH (nano) - 5%

PA6 (nano) – 10%

Five) In the same case as c), about the same composition is used, but with the following modifications:

PP random copolymer- 80%

PP-g-MAH (containing 20-25% nano powder) – 20 %

#### Step 4

This step is performed immediately following Step 3. In it, the plastic melt, which includes the mineral or ceramic sheets that have been passed through exfoliation, dispersion and homogenous mixing, is extruded from an extruder, or through an injection nozzle, into a mold, which is held at a temperature not exceeding 215°C. A tubular structure is thus produced. Air at a pressure of at least 10 bars is introduced into said tubular structure, which is stressed and pressed against the inner surface of the mold, whereby it is shaped and the orientation of the Montmorillonite platelets is completed.

Steps 3 and 4 can be carried out after the mixing of the components in the melt in a separate stage by one-screw compounder.

The results of the invention are illustrated in Figs. 6 to 11, in which are shown the losses of an organic solvent from a container made of pure polyethylene and from a container according to an example of the invention. The particular solvent to which the figures refer is xylene, but what is shown therein would be essentially shown if a different organic solvent has been used. The container according to the invention could be any container made as described in the foregoing examples, the differences between the behavior of different such containers being of the order of magnitude of experimental errors.

While examples of the invention have been given by way of illustration, it will be apparent that many modifications, variations and adaptations may be made therein by persons skilled in the art, without departing from the spirit of the invention or exceeding the scope of the claims.

### CLAIMS

1. Nanocomposite material which comprises a plastic matrix consisting of polyolefin and a mineral component in nanoparticles.
2. Nanocomposite material according to claim 1, wherein the mineral component is Montmorillonite, in particles the major part of which have the shape of platelets of a thickness of the order of magnitude of nanometers.
3. Nanocomposite material according to claim 2, wherein the length and breadth of the Montmorillonite platelets ranges from 1.5  $\mu\text{m}$  down to a few tenths of 1  $\mu\text{m}$ .
4. Nanocomposite material according to claim 2, which is formed into a product having at least one direction of orientation, and wherein the Montmorillonite platelets are mainly parallel or sub-parallel to said direction of orientation.
5. Nanocomposite material according to claim 2, wherein the amount of the Montmorillonite platelets is from 1 to 5 wt% of the total weight of the composite.
6. Nanocomposite material according to claim 1, wherein the polyolefin is HDPE or PP.
7. Nanocomposite material according to claim 6, further comprising additional polymeric materials.

8. Nanocomposite material according to claim 7, wherein the additional polymeric materials are chosen from the group consisting of functionalized polyolefins and polyamides.
9. Nanocomposite material according to claim 8, wherein the functionalized polyolefins are polyolefins grafted with maleic anhydride.
10. Process for making the nanocomposites of claim 1 or 2, which comprises the steps of:
  - a) providing a polyolefin material;
  - b) providing virgin Montmorillonite;
  - c) subjecting the Montmorillonite to intercalation;
  - d) preferably, mixing the intercalated Montmorillonite with a compatibilizer and with a polyamide to form concentrates; and
  - e) compounding the concentrates with the polyolefin material to produce the nanocomposite.
11. Process according to claim 10, comprising compounding the concentrate not only with the polyolefin material, but also with one or a plurality of additional polymeric components.
12. Process according to claim 10, further comprising compounding the polyolefin material with a polyamide.
13. Process according to claim 10, wherein the intercalation is effected by treating the Montmorillonite with an intercalator.
14. Process according to claim 10, wherein the intercalator is chosen from the group consisting of epoxy resins and silanes.

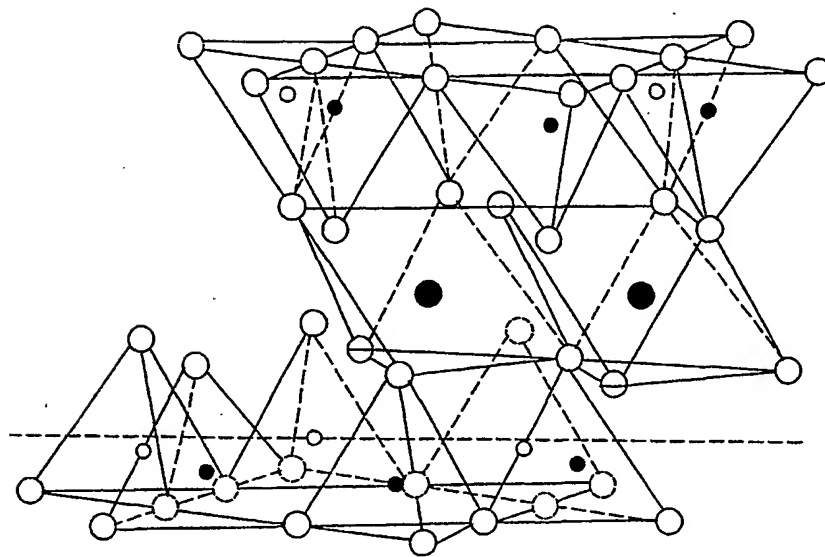
15. Process according to claim 10, wherein the intercalator is bisphenol A. epoxy resin.
16. Process according to claim 10, wherein the intercalator is brought to a condition of low viscosity.
17. Process according to claim 10, wherein the intercalation is effected by mixing the virgin Montmorillonite with a solution of the intercalator in an organic solvent.
18. Process according to claim 16, wherein the solution of the intercalator is a solution of epoxy resin in chloroform.
19. Process according to claim 10, wherein the compatibilizer is a polyolefin grafted with a functional compound.
20. Process according to claim 10, wherein the compatibilizer is a polyolefin grafted with maleic anhydride.
21. Process according to claim 10, wherein the amount of compatibilizer used is 5 to 10 wt% of the amount of the polymer matrix of the final composite.
22. Process according to claim 10, further comprising forming the nanocomposite into the final product.
23. Process according to claim 21, wherein the concentrates are compounded with the polyolefin material concurrently with the formation of the final product.

24. Process according to claim 21, wherein the final product is formed by extrusion or molding.
25. Process according to claim 23, wherein the final product is formed by extrusion blow-molding or injection blow-molding
26. Product comprising a nanocomposite according to claim 1 or 2.
27. Product having at least one axis of symmetry and formed at least mainly from a nanocomposite having a polyolefin matrix and comprising Montmorillonite platelets oriented at least in part parallel to said axis.
28. Product according to claim 26, which is a container, and wherein Montmorillonite platelets are oriented at least in part parallel to the lateral surfaces of the container.
29. Product according to claim 26, which is a sheet or a multisheet structure, and wherein the Montmorillonite platelets are mainly parallel or sub-parallel to the sheet surfaces.
30. Nanocomposites according to claim 1, further comprising a polyamide.
31. As a product, intercalated Montmorillonite platelets suitable for compounding with a polyolefin matrix.
32. Process for making intercalated Montmorillonite platelets, which comprises providing virgin Montmorillonite and treating it with an intercalator which is bisphenol A. epoxy resin in a condition of reduced viscosity.

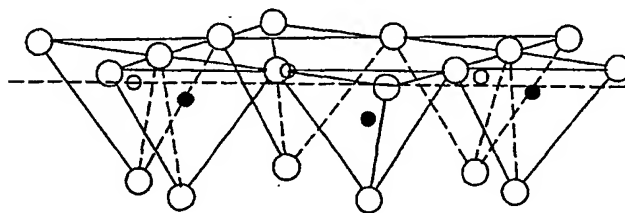


33. As a product, concentrates comprising intercalated Montmorillonite platelets mixed with a compatibilizer.
34. Polymeric compositions comprising polyolefins, Montmorillonite platelets and 5-10% of at least one polyamide.
35. Nanocomposites according to claim 1, substantially as described.
36. Process for making nanocomposites according to claim 10, substantially as described.
37. Products comprising a nanocomposite, substantially as described.

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Exchangeable cations



- ⊖ Hydroxyls
- Oxygens
- Aluminum, iron, magnesium
- and
- Silicon, occasionally aluminum

Fig. 1



Fig. 2

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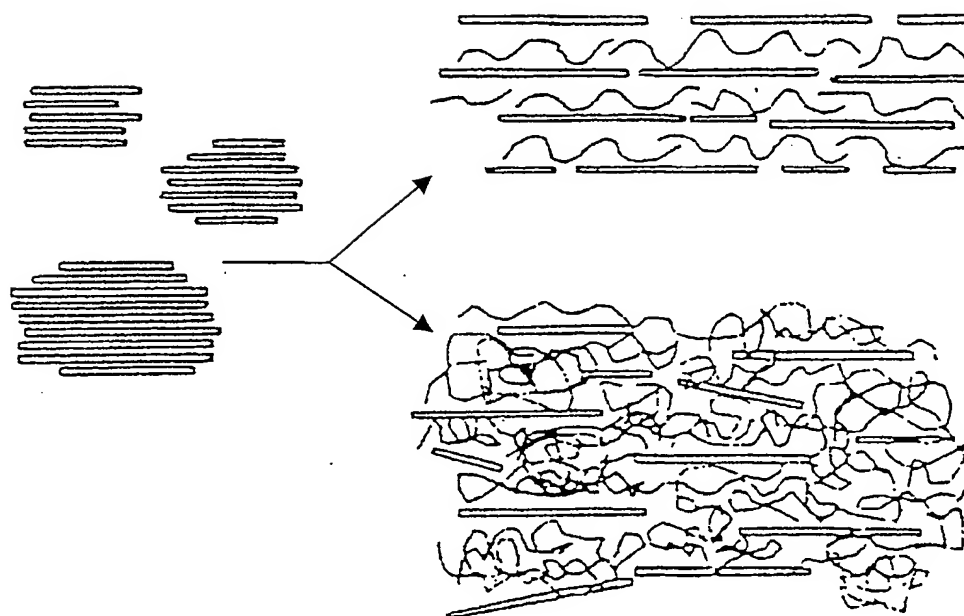


Fig. 3

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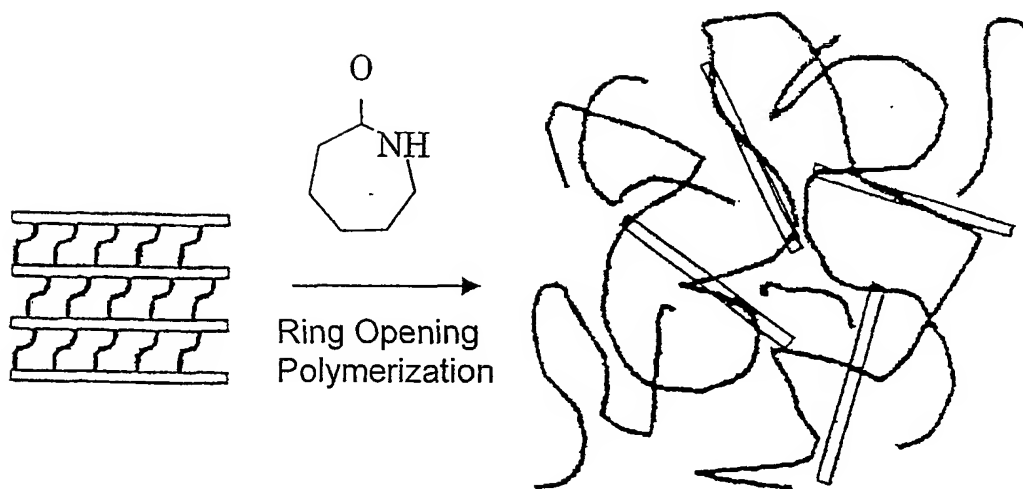


Fig. 4

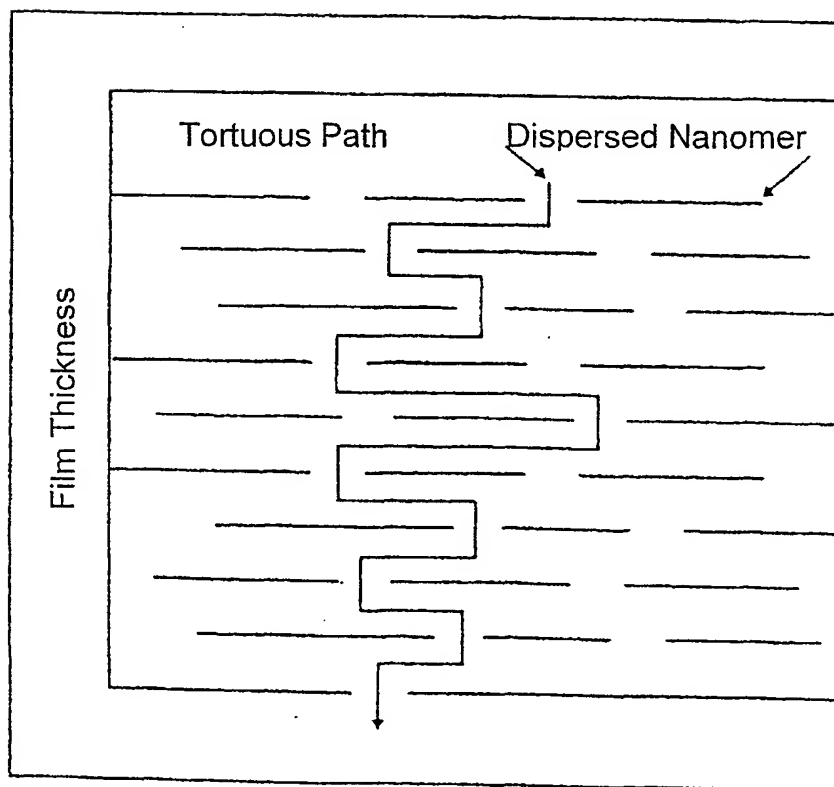


Fig. 5

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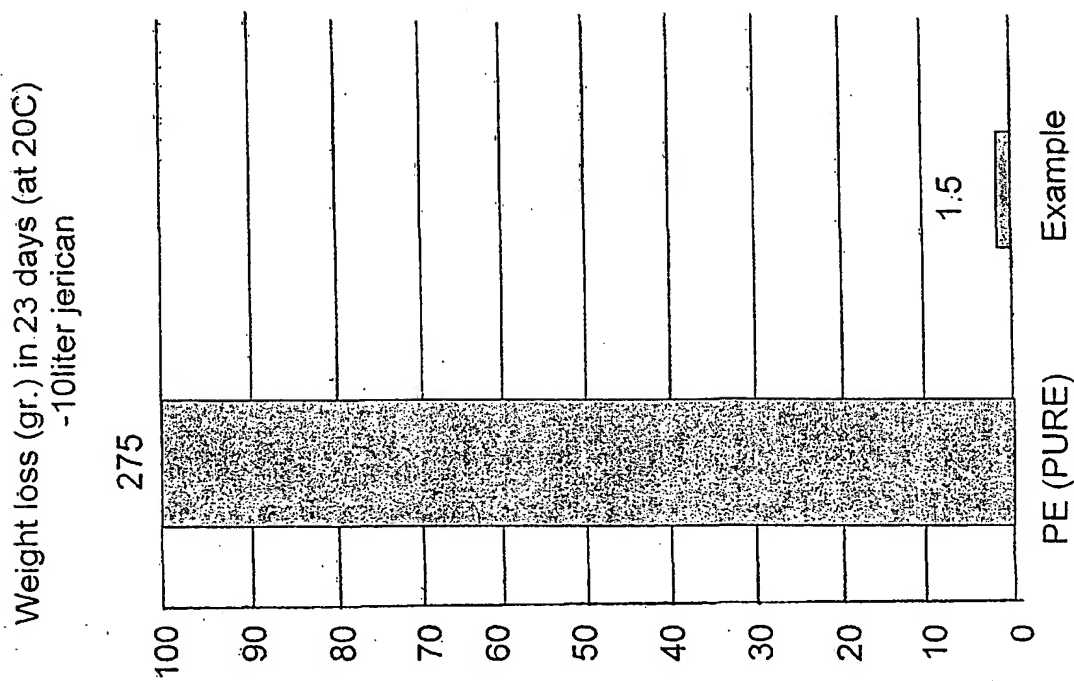


Fig. 7

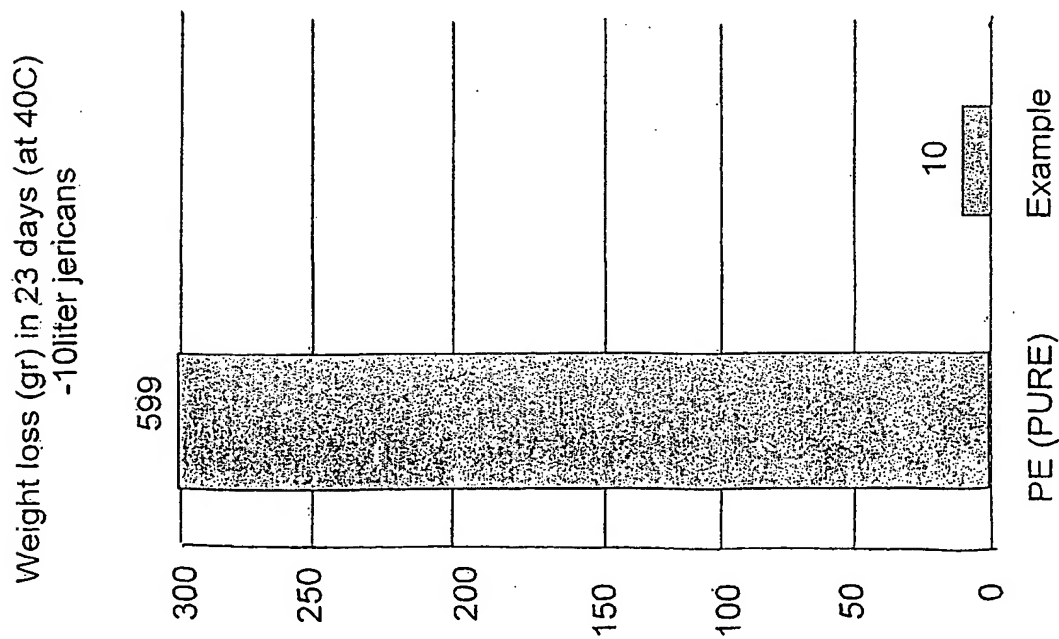


Fig. 6

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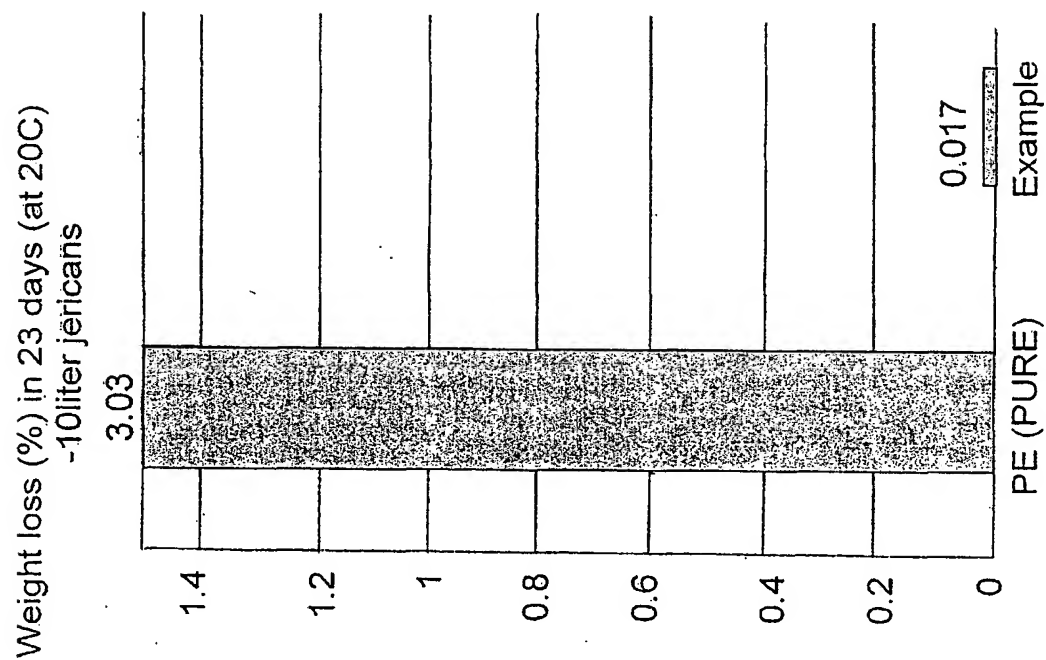


Fig. 9

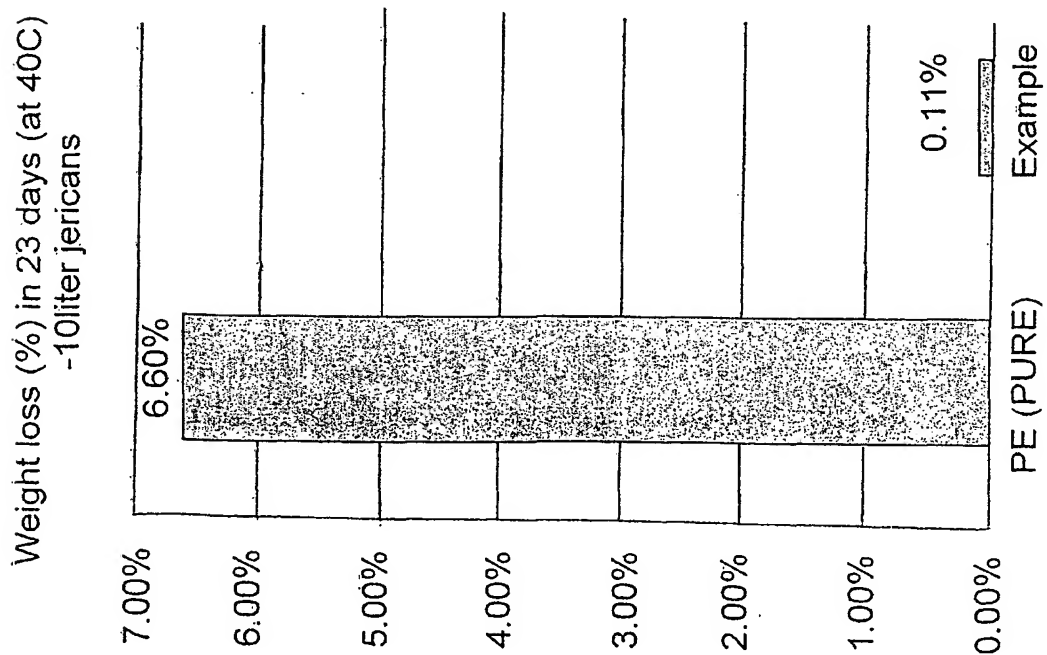


Fig. 8

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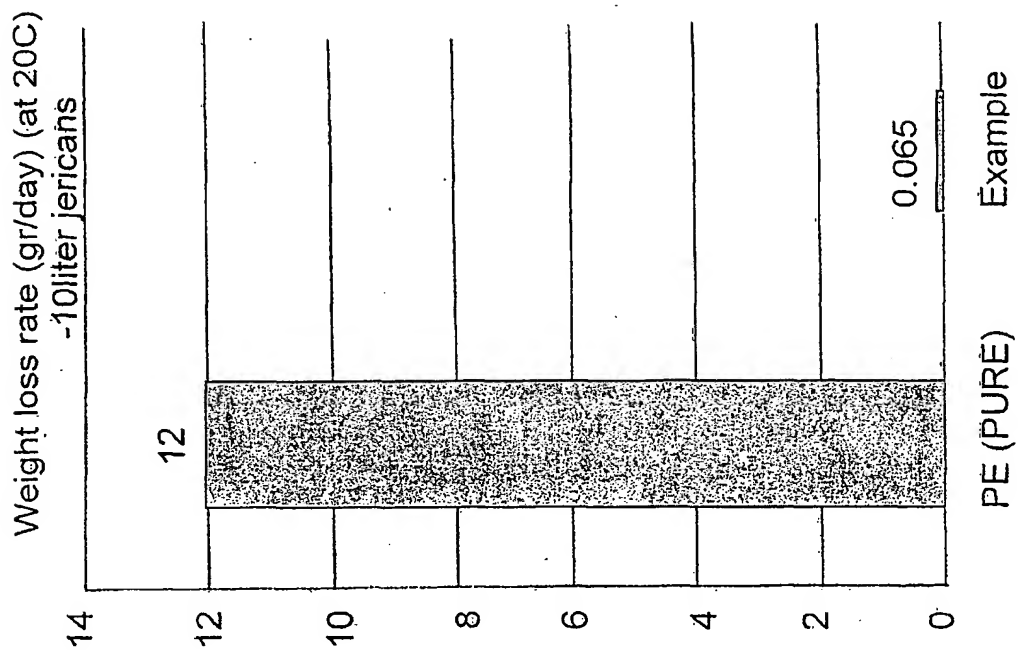


Fig. 11

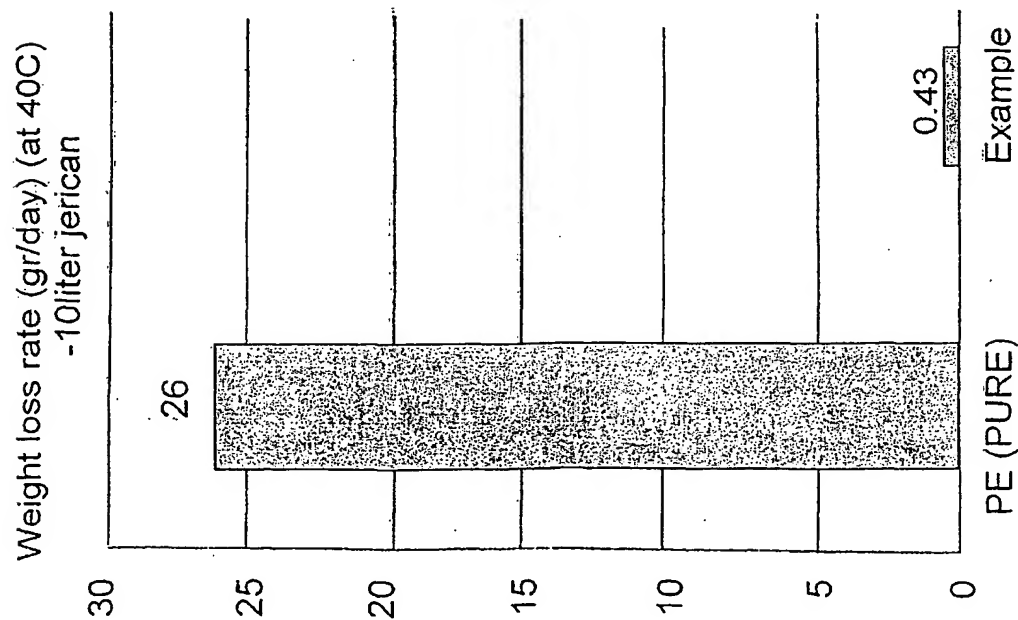


Fig. 10

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142376 2 April 2001 (02.04.2001) IL
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**WO 02/079318 A3**

(54) Title: NANOCOMPOSITES, PROCESS FOR THEIR PREPARATION AND PRODUCTS MADE THEREFROM

(57) Abstract: Nanocomposite material which comprises a plastic matrix consisting of polyolefin and a mineral component in nanoparticles. The mineral component is Montmorillonite, in particles the major part of which have the shape of platelets of a thickness of the order of magnitude of nanometers. The length and breadth of the Montmorillonite platelets may vary from 1.5 m down to a few tenths of 1 m. The Nanocomposite material may be formed into a product having at least one direction of orientation, wherein the Montmorillonite platelets are mainly parallel or sub-parallel to the direction of orientation.

# INTERNATIONAL SEARCH REPORT

Inten      Application No  
PC1/H 02/00239

A. CLASSIFICATION OF SUBJECT MATTER  
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According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>WO 01 05880 A (STEEMAN PAULUS ANTONIUS MARIA ;VOETS PATRICK ELISABETH LUC (NL); D) 25 January 2001 (2001-01-25)</p> <p>page 4, line 9 - line 24 page 4, line 33 -page 5, line 3 page 8, line 28 - line 34 page 9, line 5 - line 33 claims 1-7,9,12-14</p> <p style="text-align: center;">--- -/--</p>	<p>1-8, 10-14, 21-31, 33-37</p>

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# INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>WO 00 78540 A (TRITON SYSTEMS INC) 28 December 2000 (2000-12-28)</p> <p>page 21, line 21 - line 29 page 39, line 16 - line 25 page 40, line 16 - line 19 page 66, line 15 -page 68, line 25; example 12 claims 32,37,47,55,58,62,63</p> <p>---</p>	<p>1-14,16, 19-31, 33-37</p>
X	<p>US 5 910 523 A (HUDSON STEVEN DAVID) 8 June 1999 (1999-06-08)</p> <p>column 2, line 3 - line 8 column 4, line 20 -column 5, line 8 column 5, line 35 - line 36 claims 1,4,6,8-13</p> <p>---</p>	<p>1-10,13, 14,16, 17, 19-24, 26,27, 31,33, 35-37</p>
X	<p>WO 93 04118 A (ALLIED SIGNAL INC) 4 March 1993 (1993-03-04)</p> <p>page 30, line 3 - line 10 page 39, line 21 -page 40, line 5 example 6; table 11 example 8 claims 1-3,9</p> <p>---</p>	<p>1-8, 10-14, 16,17, 22,24, 26-31, 33-37</p>
X	<p>EP 0 995 591 A (SHOWA DENKO KK) 26 April 2000 (2000-04-26)</p> <p>claims</p> <p>---</p>	<p>1-6,10, 22-29, 31,35,37</p>
X	<p>US 5 554 670 A (GIANNELIS EMMANUEL P ET AL) 10 September 1996 (1996-09-10) claims 1,2,5</p> <p>-----</p>	<p>32,37</p>
A		<p>1,10,14, 15</p>

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/02/00239

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 0105880	A	25-01-2001	NL 1012636 C2 NL 1013520 C2 AU 6026400 A AU 6026500 A EP 1196480 A1 EP 1198496 A1 WO 0105879 A1 WO 0105880 A1	22-01-2001 22-01-2001 05-02-2001 05-02-2001 17-04-2002 24-04-2002 25-01-2001 25-01-2001
WO 0078540	A	28-12-2000	AU 5488400 A EP 1200254 A1 WO 0078540 A1	09-01-2001 02-05-2002 28-12-2000
US 5910523	A	08-06-1999	NONE	
WO 9304118	A	04-03-1993	AT 159270 T CA 2115255 A1 DE 69222773 D1 DE 69222773 T2 EP 0598836 A1 JP 2674720 B2 JP 6504810 T WO 9304117 A1 WO 9304118 A1 US 5747560 A	15-11-1997 04-03-1993 20-11-1997 12-02-1998 01-06-1994 12-11-1997 02-06-1994 04-03-1993 04-03-1993 05-05-1998
EP 0995591	A	26-04-2000	JP 2000129056 A EP 0995591 A1	09-05-2000 26-04-2000
US 5554670	A	10-09-1996	AU 3419195 A BR 9508914 A CA 2199616 A1 EP 0782593 A1 JP 10505871 T NO 971109 A WO 9608526 A1	29-03-1996 03-11-1998 21-03-1996 09-07-1997 09-06-1998 07-05-1997 21-03-1996

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